General and Pitting Corrosion Deduced from Current Oscillations and Explained in Terms of a Point Defect Model

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Passivity of iron has been the subject of numerous studies during the last two centuries. During the past decade the use of advanced *in-situ* techniques such as X-ray adsorption near edge spectroscopy (XANES) and scanning tunneling microscopy (STM) resulted in a remarkable amount of information on the composition and structure of the passive oxide film on Fe [1, 2]. It is suggested that the film has a defective structure and consists of either Fe_3O_4 or γ-Fe_2O_3.

During the anodic polarization, iron maintains passivity in a wide potential region (~1.4 V) depending on the *pH*. Breakdown of passivity and evolution of oxygen is observed at the transpassivation potential (E_{tr}), the upper potential-boundary of the passive state. On the other hand, transition of the passive iron to an active state occurs during the poalrization towards negative potentials at the Flade potential (E_F), the lower potential-boundary of the passive state [3]. It is considered that at E_F an outer layer of the Fe_3O_4 turns to γ-Fe_2O_3 through a further oxidation of Fe^{2+} to Fe^{3+}. The γ-Fe_2O_3 is the stable oxide (barrier layer) in acid solutions and the properties of the passive film are determined by this outer layer.

Fig. 1 shows a schematic plot of a typical current-potential (*I-E*) curve with the transition from the passive to active state. This transition in sulfuric acid solutions is accompanied by current oscillations in a narrow potential region (~30 mV) at $E<E_F$. The oscillations are monoperiodic of a relaxation type and consist of repeated activation/passivation events. It was observed that these oscillations change in periodicity in the presence of aggressive halide ions, such as chloride ions. A variety of complex current oscillations occur, depending on the halide ion aggressiveness [4-6]. Observations of the Fe surface reveal, during complex oscillation, pitting corrosion while, during monoperiodic oscillation, general corrosion. For example, oscillations remain monoperiodic in the presence of HF that cause general corrosion [9]. Therefore, the investigation of passive-active current oscillations provide an alternate approach to study the pitting susceptibility of the passive film formed on iron and to classify ions in terms of their aggressive or inhibitive properties. Usually, pitting is studied at $E<E_{pit}$ by analyzing electrochemical noise or at $E>E_{pit}$ (Fig. 1) (pitting potential E_{pit} is the critical potential for stable pitting to occur) [7]. It is noticed that the amplitude of noise is very low (a few nA cm^{-2}) compared with that of current oscillations (~1-2 A cm^{-2}).

In the present work it is indented to study further the oscillatory phenomena of the Fe|H_2SO_4 system by investigating the effect of other ions that are beneficial either to oxide growth or oxide dissolution. Towards this goal perchlorate, nitrate and chromate are added and the results are compared with those of previous studies where aggressive halide ions (Cl$^-$, Br$^-$, I$^-$) were added.

According to certain criteria deduced from the characteristics of current oscillations, the aggressiveness order was found to be Cl$^->$Br$^->$I$^-$. The criteria proposed previously [8] to distinguish between general and pitting corrosion are found to be valid for the effect of oxyanions used in the present study. The changes caused by adding various anions seem to be closely related to the electronic and ionic properties of the oxide film.

The growth and breakdown of the oxide film can be explained in terms of a point defect model [9]. The passive film formed on iron is considered in the present study as a defective oxide containing a high concentration of point defects, namely cation and anion (oxygen) vacancies. The cation vacancies generated at the film|solution (f|s) interface are transferred towards the metal|film (m|f) interface where they react with metal giving rise to metal holes. The oxygen vacancies generated at the m|f interface through metal holes are transferred to the f|s interface where they react with H_2O. On the basis of the physicochemical processes occurring at the m|f and f|s interfaces and through the oxide film it is deduced that the initiation of pitting involves occupation of an anion vacancy. It is also deduced that the general corrosion is associated with the formation of surface complexes between the iron cations of the oxide lattice and the solution anions.

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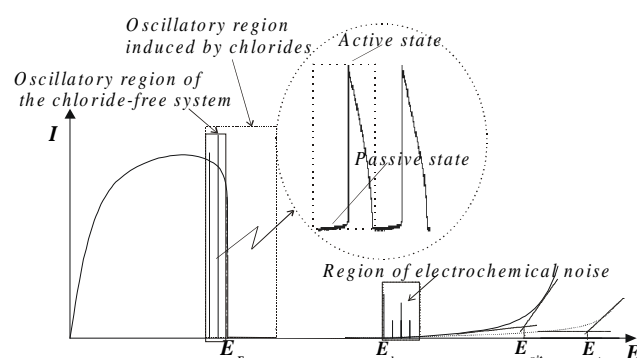[9] D.D. Macdonald, *Pure Appl. Chem.* **7**, 951 (1999).

Fig. 1: Schematic plot of the anodic *I-E* polarization curve of Fe in halide-free and halide-containing sulfuric acid solutions indicating the region investigated in this study with respect to that beyond E_{pit} (or beyond a breakdown potential E_b) used in other studies of pitting corrosion.